Short communication

Hydrogen release capacity of the LiAlH$_4$–MgH$_2$ system

Zheng Xueping [a,*], Xiao Guo [a], Ma Qiuhua [b], Liu Shenglin [a], Li Tao [a], Feng Xin [a], Zheng Jiaojiao [a]

[a] School of Materials Science and Engineering, Chang'an University, Xi'an 710061, China
[b] Materials Science and Engineering Institute, Henan University of Technology, Zhengzhou 450001, China

HIGHLIGHTS

► LiAlH$_4$–MgH$_2$ sample with the molar ratio of 1:0.5 presents the largest dehydrogenation amount.
► Doping markedly shortens the dehydrogenation time of LiAlH$_4$–MgH$_2$ sample.
► Doping improves the amount and the rate of hydrogen release of the LiAlH$_4$–MgH$_2$ sample.

ARTICLE INFO

ABSTRACT

In this work, the hydrogen release capability of the LiAlH$_4$–MgH$_2$ composite system is analyzed. Analysis of the molar ratios of LiAlH$_4$ to MgH$_2$ shows that the LiAlH$_4$–MgH$_2$ sample with the molar ratio of 1:0.5 presents the largest amount of hydrogen. Further study finds that doping with the catalysts LaCl$_3$, La$_2$O$_3$ and CeO$_2$ markedly shortens the hydrogen release time of the LiAlH$_4$–MgH$_2$ sample, except when doping with 1 mol% CeO$_2$. In addition, doping is found to significantly improve the amount and the rate of hydrogen release of the LiAlH$_4$–MgH$_2$ sample. The amount of hydrogen release by the sample doped with 3 mol% La$_2$O$_3$ reaches about 6.5 wt%, which is about 1.1 wt% higher than that of the undoped sample.

1. Introduction

Complex hydride alloys have attracted the attention of researchers in recent years because of their high-capacity hydrogen storage properties. For example, the amount of hydrogen stored by NaAlH$_4$ and LiAlH$_4$ has reached 7.4 and 10.5 wt%, respectively. Although the development of these alloys as new types of hydrogen storage alloys has been rapid, research into the reaction mechanisms of these complex hydride alloys is still in an early stage of exploration. A great deal of research has focused on improving the hydrogen absorption and release properties, with the main method being to find a better catalyst. For example, Blanchard [1] has studied Ti-based and V-based compounds. Resan [2] and other scientists have studied TiH$_2$, TiCl$_3$, TiCl$_4$, AlCl$_3$, FeCl$_3$, Fe, Ni, V, Ti and C. Furthermore, some other new catalysts have been studied, such as NH$_4$Cl [3], TiF$_3$ [4], nanofiber [5], nanonickel [6], NH$_3$ [7]. In addition, some researchers have studied the sample preparation technology in order to improve these alloys' hydrogen absorption and release properties. Some of the composite systems of complex hydride hydrogen storage alloys have attracted the attention of many researchers, with a series of such materials having been reported, such as: MAlH$_4$–NH$_4$Cl, LiAlH$_4$–MgH$_2$–TiF$_3$, LiBH$_4$–MgH$_2$, NaBH$_4$/MH$_2$ [3,8–10]. LiAlH$_4$–MgH$_2$ composite system was selected for study in the present work as this system has only recently attracted attention. The report from Zhang et al. [11] showed that the onset dehydrogenation temperature of MgH$_2$ is observed at around 250 °C, which is more than 50 °C lower than that of as-milled MgH$_2$ by LiAlH$_4$ in as-synthesized MgH$_2$–LiAlH$_4$ composites (1:1, 2:1 and 4:1 in molar ratios). The study by Vittetoe et al. on the dehydrogenation of the LiAlH$_4$–nanoMgH$_2$ material found that this system exhibited a major hydrogen weight loss of about 5.2 wt.% (∼200 °C) [12]. In this work, the dehydrogenation properties of the LiAlH$_4$–MgH$_2$ system prepared by solid-state milling and the LiAlH$_4$–MgH$_2$ system doped with LaCl$_3$, La$_2$O$_3$ and CeO$_2$ will also be studied.

2. Experimental details

The main purpose of this experiment was to study the influences of different rare earth compounds on the hydrogen release

properties of the LiAlH$_4$–MgH$_2$ composite system. LiAlH$_4$ ($\geq$98 wt% pure) and MgH$_2$ ($\geq$98 wt% pure) were used as received without additional purification. The rare earth compounds selected for the experiment were LaCl$_3$, La$_2$O$_3$ and CeO$_2$. A planetary ball mill was used with a milling time of 1 h. In order to prevent oxidation of the samples, the whole sample loading and sampling process was carried out in a glove box filled with argon. The hydrogen release properties of the samples were tested using pressure–composition–temperature (PCT) equipment. The doped LiAlH$_4$–MgH$_2$ samples were firstly heated to 200 °C, and then the properties of hydrogen release were tested at this temperature. The doping amounts of the dopants were 1, 2, 3, 4 and 5 mol%. The PCT apparatus was operated up to 10 Mpa and at 400 °C. The pressure of hydrogen released in relation to volume was displayed by a pressure transducer. The experimental studies utilized a reactor that consisted of two parts: a heater and sample vessel. The former was connected with the pressure transducer and a thermocouple. It had a 2.2 cm outside diameter (OD), 0.5 cm wall and 20 cm internal length. It was loaded with the sample vessel (1 cm OD, 0.1 cm wall and 5 cm internal length). The sample vessel was loaded with about 0.1 g of NaAlH$_4$. The reactor was heated using an air furnace. During heating, the hydrogen release from the sample vessel firstly entered the heater and then the transit pressure transducer. The value of hydrogen pressure could be clearly read. The weight percentage of hydrogen released was obtained according using a formula. It should be noted that the hydrogen was cooled to room temperature by the cooling water after it exited the sample vessel.

3. Results and discussion

3.1. Hydrogen release properties of LiAlH$_4$–MgH$_2$ system with different molar ratios

Hydrogen release was studied for different molar ratios of the LiAlH$_4$–MgH$_2$ composite system. The molar ratios of LiAlH$_4$–MgH$_2$ were 1:0.5, 1:1, 1:1.5 and 1:2. The test procedure of the samples was that the samples were firstly heated to 200 °C and kept for about 120 min at this temperature.

Fig. 1 shows the relationship between the amount and time of hydrogen release of the LiAlH$_4$–MgH$_2$ system of these molar ratios. It can be seen from the curves that when the molar ratio of LiAlH$_4$ to MgH$_2$ was 1:0.5, the sample exhibited the largest amount of hydrogen release, followed by the sample with the molar ratio of 1:1. When the molar ratios were 1:1.5 and 1:2, the amount and the

rate of hydrogen release of the samples was the same. However, compared to the samples with the molar ratio of 1:0.5 and 1:1, the starting time of hydrogen release was earlier. Therefore, in the following studies, the LiAlH$_4$–MgH$_2$ system with a molar ratio of 1:0.5 was chosen as the subject for study, and the influence of adding amounts of LaCl$_3$, La$_2$O$_3$ and CeO$_2$ on the hydrogen release properties of the system was mainly analyzed.

3.2. Influence of LaCl$_3$ on hydrogen release properties of LiAlH$_4$–MgH$_2$ composite system

In this part of the work, the influence of the amount of LaCl$_3$ on the hydrogen release property of the LiAlH$_4$–MgH$_2$ with the molar ratio of 1:0.5 was studied in detail. Fig. 2 shows the relationship between the amount and time of hydrogen release of the samples doped with 1, 2, 3, 4 and 5 mol% LaCl$_3$. It is clear that doping LaCl$_3$ brought forward the start time of hydrogen release and increased the amount of hydrogen release. With the increase in the amount of LaCl$_3$, the amount of hydrogen release gradually increased. The maximum amount of hydrogen release reached 6.2 wt% when the doping amount increased to 5 mol%, which is obviously higher than the value for the undoped sample. In order to prove whether 5 mol% was the optimum value, the hydrogen release experiment for the LiAlH$_4$–MgH$_2$ sample doped with 6 mol% LaCl$_3$ was carried out under the same conditions. The results are shown in Fig. 3. Compared to the sample doped with 5 mol% LaCl$_3$, the amount of hydrogen released by the sample doped with 6 mol% LaCl$_3$ was lower. So in the 1–6 mol% doping amount interval, the sample doped with 5 mol% LaCl$_3$ performed best.

3.3. Influence of La$_2$O$_3$ on hydrogen release properties of LiAlH$_4$–MgH$_2$ composite system

The relationship between the amount and the time of hydrogen release of the LiAlH$_4$–MgH$_2$ samples doped with 1, 2, 3, 4 and 5 mol% La$_2$O$_3$ is shown in Fig. 4. It can be seen that the start time of hydrogen release of the samples doped with La$_2$O$_3$ was about 10 min earlier than that of LiAlH$_4$–MgH$_2$. Among the samples doped with La$_2$O$_3$, the sample doped with 3 mol% La$_2$O$_3$ had the largest amount of hydrogen released. The slopes of the curves showed that the hydrogen release rate of the sample doped with 3 mol% La$_2$O$_3$ was faster than that of other doped samples and the undoped sample.
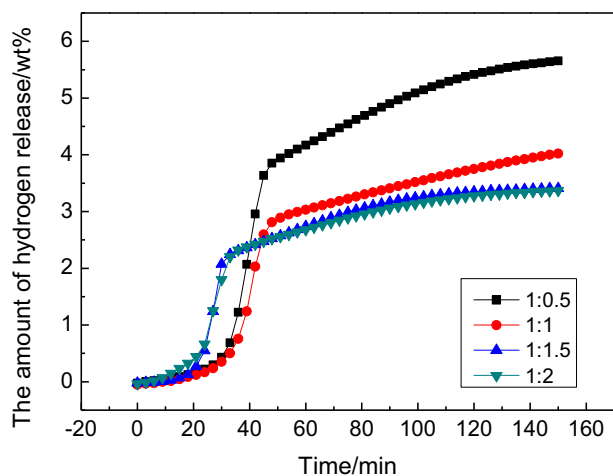

Fig. 1. The relationship between the amount and time of hydrogen release of the LiAlH$_4$–MgH$_2$ system of these molar ratios.
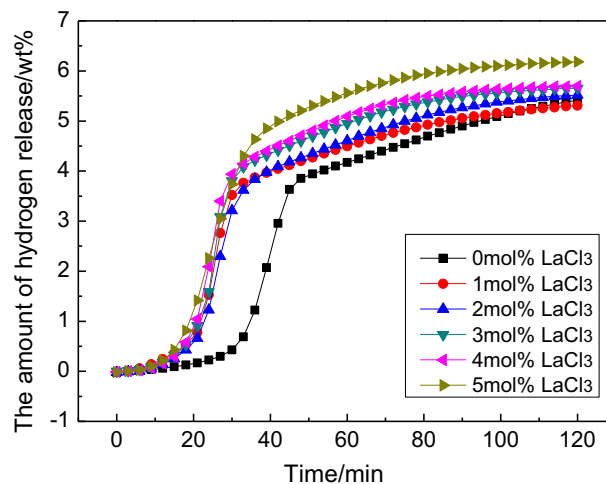

Fig. 2. The relationship between the amount and time of hydrogen release of the samples doped with 1, 2, 3, 4 and 5 mol% LaCl$_3$.
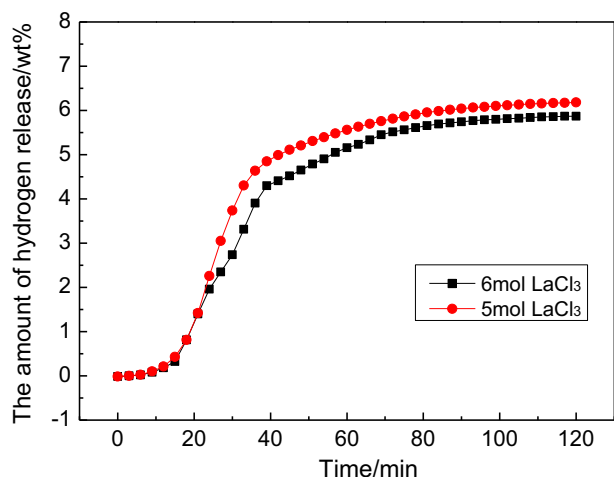
Fig. 3. The relationship between the amount and time of hydrogen release of the LiAlH$_4$–MgH$_2$ samples doped with 5 and 6 mol% LaCl$_3$.

Fig. 5. The relationship between the amount and time of hydrogen release of the LiAlH$_4$–MgH$_2$ samples doped with 1, 2, 3, 4 and 5 mol% CeO$_2$.

3.4. Influence of CeO$_2$ on hydrogen release property of LiAlH$_4$– MgH$_2$ composite system

Fig. 5 shows the relationship between the amount and time of hydrogen release of the samples doped with 1, 2, 3, 4 and 5 mol% CeO$_2$. The results show that, except for the sample doped with 1 mol% CeO$_2$, the start time of hydrogen release of the samples doped with 2–5 mol% CeO$_2$ was about 10 min earlier than that of the undoped sample. With regard to the amount of hydrogen release, this was the largest when the doping amount was 2 mol%, reaching 6.2 wt%, which is significantly larger than the value for the undoped sample. Furthermore, it can also be seen from the slope of the curves that, the rates of hydrogen release of the samples doped with CeO$_2$ were not significantly different to that for the undoped sample.

3.5. Comparison study

Fig. 6 shows the amount of hydrogen released from the LiAlH$_4$– MgH$_2$ samples doped with LaCl$_3$, La$_2$O$_3$ and CeO$_2$ versus the amount of doping. After a reduction for the sample doped with 1 mol% LaCl$_3$, the amount of hydrogen release by the samples doped with 2–5 mol% LaCl$_3$ showed a gradual increase with the increase
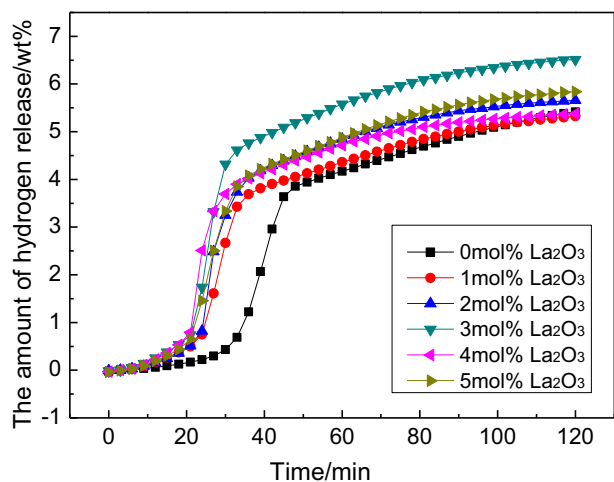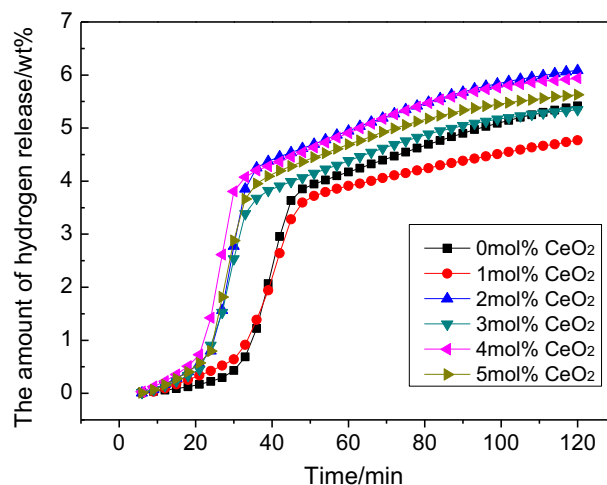
in the amount of LaCl$_3$. The largest amount of hydrogen released for the samples doped with LaCl$_3$ was about 0.8 wt% higher than that of the undoped sample. In comparison, the change in amount of hydrogen released by the samples doped with La$_2$O$_3$ and CeO$_2$ was irregular. Among the samples doped with La$_2$O$_3$, the amount of hydrogen released by the sample doped with 3 mol% La$_2$O$_3$ was the largest, reaching about 6.5 wt%, which is about 1.1 wt% higher than the value for the undoped sample. Among the samples doped with CeO$_2$, the sample doped with 2 mol% CeO$_2$ released the largest amount of hydrogen, reaching about 6.1 wt%, which is about 0.7 wt % higher than the value for the undoped sample. However, most importantly the largest dehydrogenation amount of the samples doped with LaCl$_3$, La$_2$O$_3$ and CeO$_2$ was markedly higher than that reported by other researchers, such as: Zhang et al. [11], Vittetoe et al. [12].

In order to further analyze the effect of the catalysts on the hydrogen release properties of the LiAlH$_4$–MgH$_2$ sample, the samples doped with 5 mol% LaCl$_3$, 3 mol% La$_2$O$_3$ and 2 mol% CeO$_2$ were contrasted. Fig. 7 shows the relation between the amount and the time of hydrogen release. It is very clear that the amount and the rate of hydrogen release of the sample doped with 3 mol% La$_2$O$_3$ were the largest. The start time of hydrogen release of the sample doped with 5 mol% LaCl$_3$ was the earliest, while its hydrogen release rate was the slowest.
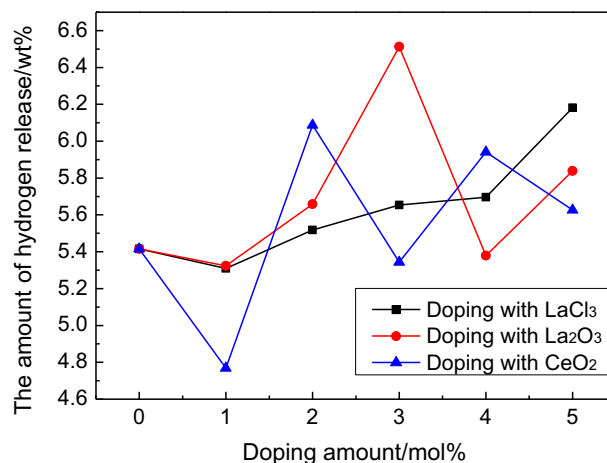

Fig. 4. The relationship between the amount and time of hydrogen release of the LiAlH$_4$–MgH$_2$ samples doped with 1, 2, 3, 4 and 5 mol% La$_2$O$_3$.

Fig. 6. The relationship between the dehydrogenation amount of the LiAlH$_4$–MgH$_2$ samples doped with LaCl$_3$, La$_2$O$_3$ and CeO$_2$ and the amount of LaCl$_3$, La$_2$O$_3$ and CeO$_2$.

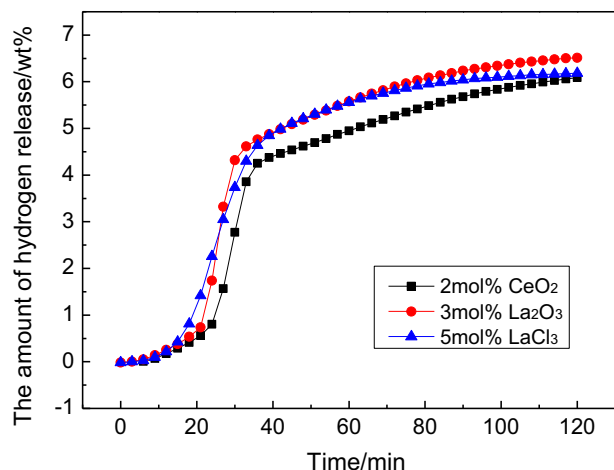**Fig. 7.** The relationship between the amount and time of hydrogen release of the LiAlH$_4$–MgH$_2$ samples doped with 5 mol% LaCl$_3$, 3 mol% La$_2$O$_3$ and 2 mol% CeO$_2$.

4. Conclusions

The study of the LiAlH$_4$ to MgH$_2$ molar ratios shows that the LiAlH$_4$–MgH$_2$ sample with the molar ratio of 1:0.5 released the largest amount of hydrogen. This sample was chosen as the object of study and hydrogen release properties of the LiAlH$_4$–MgH$_2$ samples doped with LaCl$_3$, La$_2$O$_3$ and CeO$_2$ were analyzed. With the increase in the amount of LaCl$_3$ doping, the amount of hydrogen released firstly increased and then decreased. The amount of hydrogen released by the sample was the largest when the amount of LaCl$_3$ doping was 5 mol%. In comparison, the trends in amounts of hydrogen released by the samples doped with La$_2$O$_3$ and CeO$_2$ were irregular. Among the samples doped with La$_2$O$_3$, the amount of hydrogen released by the sample doped with 3 mol% La$_2$O$_3$ was the largest, while the sample doped with 2 mol% CeO$_2$ presented the largest amount of hydrogen release among the samples doped with CeO$_2$. The largest amount of hydrogen released by these doped samples was significantly higher than that of the undoped sample. In addition, except for doping with 1 mol% CeO$_2$, doping with LaCl$_3$, La$_2$O$_3$ and CeO$_2$ shortened the start time of hydrogen release of the LiAlH$_4$–MgH$_2$ sample.

Acknowledgments

References

[1] D. Blanchard, H.W. Brinks, B.C. Hauback, P. Norby, Mat Sci. Eng. B108 (2004) 54–59.
[2] M. Resan, M.D. Hampton, J.K. Lomness, D.K. Slattery, Int. J. Hydrogen Energy 30 (2005) 1413–1416.
[3] Huajun Zhang, Yook Si Loo, Hans Geerlings, Jianyi Lin, Wee Shong Chin, Int. J. Hydrogen Energy 35 (2010) 176–180.
[4] Shu-Sheng Liu, Li-Xian Sun, Yao Zhang, Fen Xu, Jian Zhang, Hai-Liang Chu, Mei-Qiang Fan, Tao Zhang, Xiao-Yan Song, Int. J. Hydrogen Energy 34 (2009) 8079–8085.
[5] L. Hima Kumara, B. Viswanathan, S. Srinivasa Murthy, Int. J. Hydrogen Energy 33 (2008) 366–373.
[6] Robert A. Varin, Leszek Zbroniec, Tomasz Czujko, Zbigniew S. Wronski, Int. J. Hydrogen Energy 36 (2011) 1167–1176.
[7] Weifang Luo, Donald Cowgill, Ken Stewart, Vitalie Stavila, J. Alloys Compd. 497 (2010) L17–L20.
[8] Jianfeng Mao, Zaiping Guo, Xuebin Yu, Mohammad Ismail, Huakun Liu, Int. J. Hydrogen Energy 36 (2011) 5369–5374.
[9] Pattaraporn Sridechprasat, Yindee Suttisawat, Pramoch Rangsunvigit, Boonyarach Kitiyanan, Santi Kulprathipanja, Int. J. Hydrogen Energy 36 (2011) 1200–1205.
[10] S. Garroni, C. Milanese, A. Girella, A. Marini, G. Mulas, E. Menéndez, C. Pistidda, M. Dornheim, S. Suriñach, M.D. Baró, Int. J. Hydrogen Energy 35 (2010) 5434–5441.
[11] Yao Zhang, Qi-Feng Tian, Shu-Sheng Liu, Li-Xian Sun, J. Power Sources 185 (2008) 1514–1518.
[12] Andrew W. Vittetoe, Michael U. Niemann, Sesha S. Srinivasan, Kimberly McGrath, Ashok Kumar, D. Yogi Goswami, Elias K. Stefanakos, Sylvia Thomas, Int. J. Hydrogen Energy 34 (2009) 2333–2339.